

## PATENT SPECIFICATION

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NO DRAWINGS

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## COMPLETE SPECIFICATION

## Improvements in and relating to Metallised Mono-Azo Pigments and methods of making them

We, JOHNSON, MATTHEY & Co. LIMITED, a British Company of 78, Hatton Garden, London, E.C.1, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new metallised mono-azo pigments and to methods of making them.

Although a wide variety of colours ranging from yellow to maroon is obtainable from metallised azo pigments obtained by the combination of a suitable azo dyestuff with salts of such metals as calcium, barium, strontium or manganese, the majority of these pigments are in shades of red, which may vary from scarlet to crimson. It has been found that satisfactory maroon coloured pigments are difficult to obtain. Those that have been made suffer from the disadvantage that they are expensive to make or lack one or more of the essential requirements of a good pigment, such as colour strength, light fastness, freedom from bleeding, or thermal stability. Consequently, there is an unsatisfied demand for satisfactory maroon coloured pigments.

We have now discovered, according to the present invention, a class of metallised azo pigments which contain members having excellent maroon shades and which do not have the disadvantages referred to above.

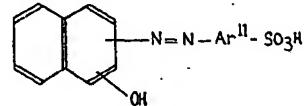
This class of pigments are compounds of one or more lanthanides or rare earth metals and an azo dyestuff obtainable by coupling a diazotised aromatic amine with a naphthol, said amine and/or naphthol having a sulphonate acid group substituent in its molecule. The term "naphthol" refers to hydroxynaphthalenes, optionally having one or more substituent groups. The azo dyestuffs referred to are in particular those of the general formula:—

Ar—N=N—Ar<sup>1</sup>

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where Ar is an aryl radical and Ar<sup>1</sup> is a naphthyl radical having a hydroxyl group in a position *ortho* to the azo group, and at least one of Ar and Ar<sup>1</sup> contains a sulphonate acid group substituent. The Ar radical preferably contains a sulphonate acid group whether or not the group Ar<sup>1</sup> has a sulphonate acid group.

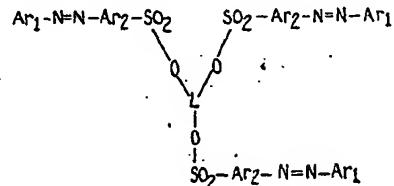
The metallised azo pigments of the invention can be regarded as lanthanide salts of one or more dyestuffs of the general formula:—



where Ar¹ is an arylene radical which can optionally contain one or more substituents, and the hydroxyl group in the naphthyl radical depicted is in a position *ortho* to the azo group.

The metallised azo pigment may also be obtained by reacting β-oxynaphthoic acid with diazotised Tobias acid, sulphanilic acid or 4B acid.

The invention also includes a metallised azo pigment which is a compound of the general formula:—



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where L is a lanthanide and Ar<sub>1</sub> and Ar<sub>2</sub> are each aromatic residues, one of the two Ar radicals attached to each azo group having a hydroxyl radical in a position *ortho* to the azo group.

The pigments of the invention can conveniently be made using the steps of reacting a solution, for instance an aqueous solution of a compound of at least one lanthanide or rare earth metal with a solution or suspension (preferably aqueous) of an azo dyestuff as above defined to cause precipitation from the mixed solutions of the pigment. In carrying out the invention in practice, the lanthanide salt solution may be added to a solution or suspension of a preformed azo dye or the latter may be prepared *in situ* by reaction of its constituents in the presence of the lanthanide salt solution. Whichever procedure be adopted the mixed reactants are conveniently boiled until the reaction of the lanthanide with the dyestuff is complete.

Whilst a compound, such as the chloride, sulphate or nitrate, of any lanthanide or rare earth metal may be used in carrying out the invention, the lanthanides of particular interest, because of their availability, are lanthanum, cerium, praseodymium and neodymium.

In order to modify the colour strength and texture of the pigment as required, a "texturising agent" such, for example, as rosin, may, in known manner, be added during the manufacture of the pigment.

Monoazo dyes suitable for use in carrying out the invention are:

- 2-naphthol - azo - 2 - naphthalene - 1 - sulphonic acid prepared by coupling  $\beta$ -naphthol and Tobias acid (2-naphthylamine-1-sulphonic acid).
- 2-hydroxy-3-naphthoic acid-azo-2-naphthalene-1-sulphonic acid prepared by coupling  $\beta$ -oxynaphthoic acid and Tobias acid.
- 2-hydroxy-3-naphthoic acid-azo-benzene p-sulphonic acid prepared by coupling  $\beta$ -oxynaphthoic acid and sulphanilic acid.
- 2-hydroxy-3-naphthoic acid-p-azotoluene-3-sulphonic acid prepared by coupling  $\beta$ -oxynaphthoic acid and 4B acid (p-toluidine-4-sulphonic acid).

The invention is illustrated by the following Examples.

**EXAMPLE 1**

An azo dye (cerium lithol maroon) is first prepared in the following manner:—

22.6 gm. of 2-naphthylamine-1-sulphonic acid (Tobias acid) and 5.0 gm. of sodium hydroxide are dissolved in 120 ml. of water.

This solution is diluted with water to increase the volume to 300 ml. and then cooled to 0°—5°C by the addition of ice. To this cold solution is then added 27 gm. of hydrochloric acid (specific gravity 1.18) and the solution again cooled in the same manner as before.

The acid solution formed as above is then diazotised by addition of a solution of 7.5 g.m. of sodium nitrite to 35 ml. of water and the mixture stirred for  $\frac{1}{2}$  hour. During this operation, the temperature of the solution is maintained at below 10°C and the pH thereof at a value of about 2. The sodium nitrite, hydrochloric acid and Tobias acid in the solution react to form an insoluble precipitate composed of the diazonium salt of Tobias acid, which is removed by filtration, washed with water at 0°—5°C and then dispersed in 300 ml. of water at 0°—10°C.

The diazonium salt formed as above is now coupled with  $\beta$ -naphthol in a solution prepared by dissolving 14.5 gm of  $\beta$ -naphthol and 4.0 gm. of sodium hydroxide in 30 ml. of boiling water and then diluting to 500 ml. with further water. The suspension of the diazonium salt is poured into the above  $\beta$ -naphthol solution over a period of 30 minutes stirring the mixture for 1 hour and then raising to the boil.

There is now slowly added to the dye suspension a solution of 12 gm. of cerium chloride ( $\text{CeCl}_3 \cdot 5\text{H}_2\text{O}$ ) in 50 ml of water over a period of about 30 minutes. The mixture so formed is then stirred for 15 minutes and then boiled for 1 hour. A maroon coloured pigment is thereby precipitated, removed by filtration, washed free from chloride and dried at 80°C.

The cerium chloride may, however, if desired, be added at any stage prior to or simultaneously with formation of the azo dyestuff. The following Example illustrates the addition of the cerium chloride simultaneously with azo dyestuff formation.

**EXAMPLE II**

9.3 gm. of the ammonium salt of 93% "2B Acid" (2-chloro-4-toluidine-5-sulphonic acid) is dissolved in 250 ml. of water. The temperature of the solution is then brought to 0°—5°C by the addition of ice and then 11 gm. of hydrochloric acid are added to the solution with constant stirring. The "2B Acid" is then diazotised by the gradual addition over a period of 30 minutes, of 2.6 gm. of sodium nitrite dissolved in 20 ml. of water and the suspension of diazonium salt so formed is maintained at a temperature of below 10°C again by the addition of ice. The diazonium salt is then filtered off and washed with 50 ml. of water and the residue dispersed in 300 ml. of water at 0°—10°C.

7.3 gm. of  $\beta$ -oxynaphthoic acid (i.e. 3-carboxy-2-hydroxy naphthalene) and 4 gm. of sodium hydroxide are dissolved in 30 ml. of hot water and the solution then diluted with 300 ml. of cold water. A solution consisting of 7 grams of rosin and 0.9 grams of sodium hydroxide in 30 ml. of water was

then added to the  $\beta$ -oxynaphthoic acid solution.

5 15 gm. of cerium chloride ( $\text{CeCl}_3 \cdot 5\text{H}_2\text{O}$ ) is then dissolved in 100 ml. of water and the solution slowly poured over a period of 15 minutes into the  $\beta$ -oxynaphthoic acid/rosin solution previously prepared.

10 The suspension of the diazonium salt is then slowly added over a period of  $\frac{1}{2}$  hour, to the boiling solution of  $\beta$ -oxynaphthoic acid/cerium chloride and rosin, the mixture stirred for 3 hours and acidified with 4.8 g. of acetic acid to give a pH of less than 3. The mixture is then boiled for 1 hour to precipitate completely the maroon pigment, which is removed by filtration, washed with water to free it of chloride and finally dried at  $80^\circ\text{C}$ . The resulting maroon pigment is found to possess the advantageous properties of light fastness (7-8 on Blue Wool Scale), thermal stability at  $200^\circ\text{C}$ , non-bleeding in xylol and white spirit and gives a bright and deep maroon in self-colour.

WHAT WE CLAIM IS:—

25 1. A metallised azo pigment which is a lanthanide derivative of a mono-azo dyestuff which dyestuff is obtainable by coupling a diazotised aromatic amine with a naphthol, said amine and/or naphthol having a sulphonic acid group substituent in its molecule.

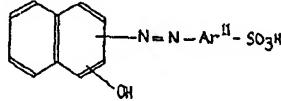
30 2. A metallised azo pigment which is a compound of a lanthanide and an azo dyestuff of the formula:



35 where Ar is an aryl radical and  $\text{Ar}^1$  is a naphthyl radical having a hydroxyl group in a position *ortho* to the azo group, and at least one of Ar and  $\text{Ar}^1$  contains a sulphonic acid group substituent.

40 3. A metallised azo pigment according to claim 2, in which the Ar radical contains a sulphonic acid group substituent.

45 4. A metallised azo pigment which is a lanthanide salt of one or more dyestuffs of the formula:



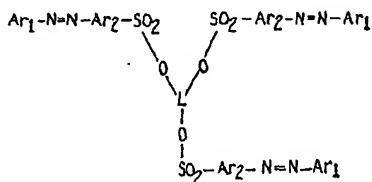
50 where  $\text{Ar}^{11}$  is an arylene radical which can optionally contain one or more substituents, and the hydroxyl group in the naphthyl radical depicted is in a position *ortho* to the azo group.

5. A metallised azo pigment according to claim 4 in which the azo dyestuff has been obtained by the reaction of  $\beta$ -naphthol with

Diazotised Tobias Acid, sulphanilic acid or "4B Acid".

6. A metallised azo pigment according to claim 4, in which the azo dyestuff has been obtained by the reaction of  $\beta$ -oxynaphthoic acid with diazotised Tobias Acid, sulphanilic acid or "4B Acid".

7. A metallised azo pigment which is a compound of the general formula:



where L is a lanthanide and  $\text{Ar}_1$  and  $\text{Ar}_2$  are each aromatic residues, one of the two  $\text{Ar}$  radicals attached to each azo group having a hydroxyl radical in a position *ortho* to the azo group.

8. A metallised azo pigment according to any of the preceding claims in which the lanthanide is lanthanum, cerium, praseodymium or neodymium.

9. A metallised azo pigment according to any of the preceding claims which is maroon in colour.

10. A metallised azo pigment which is a lanthanide compound according to claim 1 substantially as described herein with reference to the Examples.

11. The metallised azo pigment obtained as product of either of the Examples.

12. A method of making a metallised azo pigment claimed in claim 1, in which there is reacted together a solution of a compound of at least one lanthanide with a solution or dispersion of the appropriate azo dyestuff and the resulting precipitate of the metallised pigment is collected.

13. A method of making the metallised azo pigment claimed in claim 1, in which there is reacted together the appropriate diazotised aromatic amine and naphthol in the presence of a salt of a lanthanide and the resulting precipitate of the metallised azo claimed is collected.

14. A method according to claim 12 or 13, substantially as described herein.

15. A method for the preparation of lanthanide pigments, substantially as described in either of the Examples.

16. A metallised azo pigment which is a lanthanide compound obtained by the method of any of claims 12 to 15.

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